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SOURCES AND HUMAN EXPOSURE IMPLICATIONS OF CONCENTRATIONS OF ORGANOPHOSPHATE FLAME RETARDANTS IN DUST FROM UK CARS, CLASSROOMS, LIVING ROOMS, AND OFFICES

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Abstract

Concentrations of a number of organophosphate flame retardants (PFRs) were measured in floor dust collected from UK living rooms (n=32), cars (n=21), school and child daycare centre classrooms (n=28), and offices (n=61). While concentrations were overall broadly within the range of those reported previously for North America, Japan, and other European countries, median concentrations of TCIPP in all UK microenvironments exceeded those reported elsewhere in the world. Moreover, concentrations of TCIPP and TDCIPP in 2 UK car dust samples were – at 370 μg g^{-1} and 740 μg g^{-1} respectively – amongst the highest reported globally in indoor dust to date. Consistent with this, concentrations of TDCIPP in dust from UK cars exceed significantly those detected in the other microenvironments studied. Concentrations of EHDPP were shown for the first time to be significantly higher in classroom dust than in samples from other microenvironments. When compared to concentrations of PBDEs determined previously in the classroom dust samples; concentrations of all target PFRs exceeded substantially those of those PBDEs that are the principal constituents of the Penta- and Octa-BDE formulations. Moreover, while mass-based concentrations of BDE-209 exceeded those of most of our target PFRs, they still fell below those of TCIPP and EHDPP. In line with a previous observation in Sweden that indoor air contamination with TNBP was significantly lower in newer buildings; concentrations of TNBP in classroom dust were significantly higher in older compared to more recently-constructed schools. Consistent with the reported extensive use of TCIPP and TDCIPP in polyurethane foam, the highest concentrations of both TCIPP and TDCIPP in the classrooms studied, were observed in rooms containing the highest numbers of foam chairs (n=31 and 18 respectively). Exposure to PFRs of both adults and young children via ingestion of indoor dust was estimated. While even our high-end exposure estimate for young children was ~100 times lower than one previously reported health-based limit (HBLV) value for TCIPP; the margin of safety was only 5-fold when compared to another HBLV for this contaminant.

Keywords

PFRs;

Contamination;

School Dust;

House Dust;

Children's Exposure

Introduction

Recent restrictions within the EU on the use of polybrominated diphenyl ethers (PBDEs), without concomitant relaxation on fire retardancy regulations has led to an increased focus on alternative flame retardants. One such alternative are organophosphate flame retardants (PFRs), where in the US, the detection frequency of tris(1,3-dichloroisopropyl)phosphate (TDCIPP) in domestic sofas increased significantly from 24% detection in items purchased prior to 2005 to 52 % in those bought post-2005 (Stapleton et al, 2012). PFRs have a wide range of uses. Along with TDCIPP, triphenyl phosphate (TPHP) and tris(2-chloroisopropyl)phosphate (TCIPP) have been used substantially to flame retard foam upholstery in cars, as well as in domestic and office applications. Moreover, non-chlorinated organophosphates like tri-n-butyl-phosphate (TNBP) are used mainly as plasticisers (Marklund et al, 2003). As PFRs are used as additive rather than reactive FRs, their emission from treated products is comparatively facile and their presence in indoor dust from countries such as Belgium, Germany, Japan, the Netherlands, Norway, Sweden, and the US has been reported (inter alia Van den Eede et al, 2011; Brommer et al, 2012; Kanazawa et al, 2010; Brandsma et al, 2014; Cequier et al, 2014; Bergh et al, 2011b; Dodson et al, 2012)

To date, studies of the adverse health effects of PFRs are scarce, thereby hampering complete understanding of their toxicity. The currently available data were reviewed recently (Van der Veen and de Boer, 2012) indicating that chlorinated alkyl phosphates are suspected carcinogens, with other effects also reported. These include: reduced thyroid hormone levels for TDCIPP (Meeker and Stapleton, 2010); contact dermatitis (Camasara and Serra-Baldrich, 1992) and links with altered hormone levels and decreased semen quality for TPHP (Meeker and Stapleton, 2010); neurotoxicity for TDCIPP (Dishaw et al (2011), tris(2-chloroethyl) phosphate (TCEP) (Umezu et al, 1998), and tri-cresylphosphate (TMPP) (Bolgar et al, 2008); haemolytic effects for 2-ethylhexyl diphenyl phosphate (EHDPP) (Jonsson and Nilsson, 2003); and increased risk of mucosal symptoms of sick housing syndrome linked with higher indoor concentrations of TNBP (Kanazawa et al, 2010).

While the presence of brominated flame retardants (BFRs) such as PBDEs has been characterised extensively in indoor dust from a variety of UK microenvironments (Harrad et al, 2008; Harrad et al, 2010), as yet no data exist on concentrations of PFRs in UK indoor dust. This study therefore determines concentrations of PFRs in samples of dust from UK cars, classrooms, living rooms, and offices. To our knowledge, our study represents the broadest survey to date of PFRs in dust from microenvironment categories relevant to human exposure, as well as being the largest survey of PFRs in offices. Our data are compared to values from other countries and used to derive estimates of exposure of UK adults and young children to PFRs via dust ingestion. These exposure estimates are compared with appropriate health-based limit values (HBLVs). To evaluate the level of UK indoor contamination with PFRs relative to that of PBDEs, we compare concentrations of PFRs with those of PBDEs detected in the same samples of classroom dust. Finally, we examine our data for relationships between putative sources and concentrations of PFRs in our dust samples.

Materials and methods

Sampling Samples of settled dust were collected in 2011 and 2012 using previously reported methods (Harrad et al, 2008) from cars (n=21), living rooms (n=32), and offices (n=61) from a variety of locations within the West Midlands conurbation in the UK. In brief, samples were collected by vacuuming a specified area of floor (1 m2 if carpeted, 4 m2 if bare floor) for a specified period of time (1 min if carpeted, 4 mins if bare floor). Dust was retained by a nylon "sock" (25 μm mesh size), inserted in the furniture attachment of the vacuum cleaner. In addition, we analysed archived samples of dust collected in 2007-08 from UK primary school and child daycare centre classrooms (n=28) for which concentrations of other contaminants - including PBDEs - have been reported (Harrad et al, 2010). Following collection, samples were passed through a 500 μm mesh sieve prior to analysis.

102 *Analysis* Based on their relative abundance in previous studies, the following PFRs were targeted:
103 TDCIPP, TCIPP, TPHP, TNBP, EHDPP, TCEP, and TMPP. We originally targeted tris(2-
104 butoxyethyl) phosphate (TBEOP) also. However, the comparatively high blank values we observed
105 coupled with the highly variable concentrations we determined in initial evaluations of accuracy,
106 which mirrored similar reports by other authors (Brandsma et al, 2013), meant that it was excluded
107 from this study. Concentrations were determined via GC-MS in accordance with methods reported
108 previously (Brommer et al, 2012). Briefly, dust samples (50 mg, accurately weighed), were treated
109 with 100 ng each of d_{15}-TPHP and d_{27}-TNBP as internal (or surrogate) standards, and extracted via
110 vortexing, sonication, and centrifugation with three successive aliquots of hexane:acetone (3:1 v/v,
111 2 mL). The combined extracts were reduced using a gentle stream of N_2 to incipient dryness and
112 reconstituted with 1 mL hexane prior to elution through a pasteur pipette containing 1 g Florisil.
113 Following initial elution with hexane (8 mL, fraction not analysed), PFRs were eluted with ethyl
114 acetate (10 mL). This second fraction was reduced to incipent dryness under a stream of N_2 prior to
115 reconstitution with 100 µL of 1 ng/µL triamylphosphate (TAP) in iso-octane as recovery
116 determination (or syringe) standard. Final sample extracts were analysed via GC-EIMS using an
117 Agilent 5975C MSD fitted with a DB-5ms column (30 m, 0.25 mm id, 0.25 µm film thickness). The
118 GC temperature programme was 90 ˚C, hold for 1.25 min, ramp 10 ˚C/min to 170 ˚C, ramp 5
119 ˚C/min to 240 ˚C, hold for 10 min, ramp 20 ˚C/min to 310 ˚C, hold for 10 min. The mass
120 spectrometer was operated in selected ion electron ionisation mode, with Table SD-1 listing the ions
121 monitored for each targeted compound.
122
123 Purchased standards of TCIPP, TDCIPP and TMPP contained different isomers. The commercial
124 TCIPP mixture consists of 3 different isomers. As the third eluting isomer has a markedly lower
125 response than the others, it can only be seen at higher concentrations. Due to this fact, it is common
126 practice to report TCIPP levels as a sum of the 1st two eluting isomers only (referred to as TCIPP 1
127 and TCIPP 2) (Brandsma et al., 2013). This practice is adopted in this study. Where elevated

128 concentrations of TCIPP were present, TCIPP 3 was used as an additional quality control step to
129 confirm the elevated TCIPP concentration in the sample but this isomer is not reported. The
130 commercial TDCIPP mixture consists of 2 different isomers with both reported. Hence reported
131 TDCIPP concentrations in this study are the sum of both isomers. Similarly, four different peaks are
132 distinguishable (referred to as TMPP 1, 2, 3, and 4) in the commercial TMPP mixture when
133 analysed via GC. TMPP concentrations in this study are therefore reported as the sum of these 4
134 peaks.
135
136 *QA/QC* One aliquot of SRM2585 (NIST, organics in dust) was analysed with every batch of 10 dust
137 samples. As the UK samples were analysed as part of a larger study, overall 56 aliquots of
138 SRM2585 were analysed. Table SD-2 illustrates the high reproducibility of our method with
139 relative standard deviations ranging between 6.4% and 14% for individual PFRs. Neither certified
140 or indicative values for our target PFRs are provided by NIST. However, Table SD-2 compares our
141 data with the average$\pm\sigma_n$ values reported for SRM2585 in a recent report on an interlaboratory trial
142 of PFR analysis in environmental samples (Brandsma et al, 2013). The good agreement between
143 our reported concentrations and those reported in the interlaboratory trial are evidence of the
144 accuracy of our data.
145
146 At least one blank was run with every sample batch (thus every 6^{th} sample was a blank). Overall, as
147 this UK study was part of a larger project analysing PFRs in dust, a total of 107 blanks were run. A
148 blank sample consisted of pre-baked Na_2SO_4 treated as sampled dust. In addition, field blanks were
149 collected. These consisted of pre-baked Na_2SO_4, taken to the sampling location, spread on
150 aluminium foil and vacuumed as a normal sample. Acceptable blank concentrations were deemed
151 those where the concentration of the target analyte was less than 5% of the lowest concentration in
152 that batch. Where the analyte concentration in the blank fell between 5% and 20% of the
153 concentration in samples from that batch, concentrations were corrected accordingly via subtraction

of the blank concentration. If blank concentrations exceeded 20% of those in samples from the same batch, all samples in that batch were discarded and reanalysed. Concentrations of TNBP, EHDPP, TDCIPP and TMPP were below detection limits in all blank samples analysed. In contrast, low levels of TCEP (median = 0.023 μg g^{-1}), TCIPP (median = 0.03 μg g^{-1}), and TPHP (median 0.006 μg g^{-1}) were detected in a small proportion of blanks. Where appropriate, correction for these blank levels was conducted.

Results and discussion

Concentrations of PFRs in UK indoor dust

A statistical summary of the concentrations of PFRs in all samples analysed in this study is provided as Table 1, alongside data from other studies elsewhere in the world. Concentrations of PFRs in individual samples analysed in this study are provided as Table SD-3. PFRs were detected in all samples, with TCIPP relatively abundant in all microenvironments, with EHDPP, TDCIPP, and TPHP also featuring strongly in one or more microenvironments. In general, concentrations in this study are broadly similar in magnitude (i.e. μg g^{-1} levels) to those reported elsewhere in the world, with some differences in the relative abundance of individual PFRs in UK samples compared to those from other countries. Particularly noticeable, is that the maximum concentrations of both TDCIPP (at 740 μg g^{-1}) and TCIPP (370 μg g^{-1}) detected in two UK car dust samples are amongst the highest reported to date in indoor dust from any microenvironment anywhere in the world.

In living room dust (the microenvironment for which there exists by far the most information), the UK is in line with Japan and other European countries inasmuch as TCIPP is the predominant PFR. This contrasts with North America, where TDCIPP and TPHP are the most abundant. We are aware of only three other studies in which a range of PFRs have been measured in office dust (the US study of Carignan et al (2013) reported TDCIPP only). Comparison with the data for the two other European studies, reveals TDCIPP to be far less abundant in UK offices compared to Sweden

(Bergh et al, 2011b); with the low relative abundance of this PFR in UK office dust, more in line with our previous observations in German offices (Brommer et al, 2012). In UK offices, TCIPP is most abundant, followed by EHDPP, TPHP, and TCEP. Absolute concentrations of PFRs in offices in this study are overall more consistent with those in Germany and Sweden, than those reported recently for Egyptian offices (Abdallah and Covaci, 2014).

A similarly low relative abundance of TDCIPP was observed in UK classrooms, where the predominant PFR was EHDPP, followed by TCIPP, TPHP, and TCEP. This contrasts with the pattern in the only two other studies (in Norway and Sweden) of classroom dust, which both show a greater relative abundance of TDCIPP, and in Sweden, a predominance of TCEP (Bergh et al, 2011b; Cequier et al, 2014). More data exist for car dust against which our UK data can be compared. Salient observations for this microenvironment category are that UK cars are amongst the most contaminated studied to date, and that while based on its median concentration, TCIPP is the most abundant of our target PFRs in UK cars, TDCIPP is almost equally abundant. While we detected similar absolute concentrations of TDCIPP in German cars (Brommer et al, 2012), TCIPP is comparatively more abundant in UK cars, suggesting that both of these chlorinated PFRs are applied broadly equally in UK vehicles. Overall, such differences are likely attributable to international variation in the specific applications of different PFRs, along with temporal trends in a fast moving commercial and regulatory environment.

Differences in PFR concentrations in dust from different microenvironments

Figure 1 provides a visual comparison of the average concentrations for individual targeted PFRs in samples from the four different microenvironment categories studied. Using IBM SPSS Statistics for Mac (version 22.0.0.0), we applied ANOVA with Tukey post-hoc test to evaluate the hypothesis that significant differences exist between concentrations of individual PFRs in dust from different

205 microenvironment categories. As visual inspection and a Kolmogorov-Smirnov test revealed the
206 data were not normally distributed, concentrations were log-transformed prior to ANOVA.
207
208 Concentrations of TDCIPP in car dust exceeded significantly ($p<0.001$) those in classroom, living
209 room and office dust, while those of EHDPP in classroom dust exceeded significantly ($p<0.001$)
210 those detected in all the other microenvironments studied. EHDPP has found wide application in
211 PVC, rubber, polyurethanes, and paints (Environment Agency, 2009); thus there appears a likely
212 greater abundance of such items in classrooms than in cars, homes or offices. Our findings for
213 TDCIPP are consistent with the highly elevated concentrations of TDCIPP in dust sampled from car
214 seats in the Netherlands, that far exceeded those in house dust in the same study (Brandsma et al,
215 2014). They are also in partial agreement with a study in Boston, USA, where concentrations of
216 TDCIPP in car and office dust exceeded those in house dust (Carignan et al, 2013). It has been
217 reported that TDCIPP is used only in applications requiring a particularly high degree of flame
218 retardancy owing to its higher price compared to TCIPP, and that the majority of TDCIPP is used in
219 polyurethane foams employed in vehicles (EU, 2008). We could find no significant relationship
220 between concentrations of any of our target PFRs in dust and the age of the vehicle.
221
222 *Do concentrations of PFRs in classroom dust exceed those of PBDEs?*
223 While we did not determine concentrations of PBDEs in dust samples collected specifically for this
224 study, such information is available for the archived classroom dust samples (Harrad et al, 2010).
225 Figure 2 illustrates that concentrations of the principal PBDE congeners found in the Penta-BDE
226 and Octa-BDE formulations (BDE-99 and BDE-183) are substantially lower than each of the PFRs
227 targeted in this study, with the difference especially marked for TCIPP, TDCIPP, and EHDPP. This
228 finding is consistent with recent reports both from the US (Dodson et al, 2012) and elsewhere in
229 Europe (Van den Eede et al, 2011). In contrast, likely arising from the extensive use of the Deca-
230 BDE product in the UK, concentrations of BDE-209 in our classroom dust samples generally

231 exceed those of all target PFRs except for TCIPP and EHDPP. We highlight however that when the
232 molecular mass of PBDEs and PFRs are taken into account, concentrations of BDE-209 and TCIPP
233 in our classroom samples are broadly similar when reported on a molar basis – i.e. expressed as
234 μmol/g. As these classroom samples were collected in 2007-08, we hypothesise that this general
235 predominance of PFRs over PBDEs will be greater in more recent samples, given the recent
236 restrictions on manufacture and new use of PBDEs.
237
238 *Influence of building age on PFR concentrations in UK classroom dust*
239 The influence of building age on PFR concentrations in UK classroom dust was tested by subjecting
240 log-transformed data to ANOVA with a Tukey post-hoc test. Buildings were classified into 5 age
241 categories: pre-1960 (n=7), 1960-1979 (n=4), 1980-1979 (n=7), 1990-1999 (n=5) and 2000-2008
242 (n=4). Concentrations of TNBP were significantly different ($p<0.05$) between the different building
243 age categories. Pre-1960 schools had the highest average concentrations (0.27 μg g^{-1}), followed by
244 1960-1979 (0.22 μg g^{-1}), 1980-1989 (0.20 μg g^{-1}), 1990-1999 (0.07 μg g^{-1}), and 2000-2008 (0.06 μg
245 g^{-1}). This increase in TNBP contamination with increasing building age is consistent with a similar
246 observation for TNBP in air in Swedish apartment buildings (Bergh et al, 2011a), and suggests that
247 TNBP is not being used as a substitute FR for restricted BFRs. No other significant influences of
248 building age on PFR concentrations were evident.
249
250 *Influence of room contents on concentrations of PFRs in UK dust*
251 To examine the influence of room contents on PFR concentration in UK classroom dust, multiple
252 linear regression analysis was performed (IBM SPSS Statistics for Mac version 22.0.0.0, automatic
253 linear modelling) using log transformed PFR concentrations as the dependent variable and numbers
254 of putative sources as independent variables. The significance level applied was $p<0.05$. Putative
255 sources for which data were collected via questionnaire at the time of sampling included (as
256 appropriate to the microenvironment examined): numbers of foam containing chairs/sofas/child car

seats, PCs, TVs, electronic devices, and the presence or absence of carpet. No significant relationships were discernible for dust from cars, classrooms, and offices. Moreover, PFR concentrations in living room dust were not significantly correlated with numbers of foam chairs or PCs, nor the presence of curtains or carpet. Given the range of different flame retardants used in UK consumer items, this is likely attributable to source misclassification, and some indication of a likely factor influencing PFR concentrations in our dust samples, is given by the fact that the highest concentrations of both TCIPP and TDCIPP in the classrooms studied, were observed in rooms containing the highest numbers of foam chairs (n=31 and 18 respectively). Conversely, the existence of PFR sources for which data were not collected in this study, are indicated by the fact that the classroom containing the highest concentration of TCEP, the second highest concentration of TDCIPP, and the third highest concentration of TCIPP; contained no foam chairs, no carpet, and only 1 PC and 1 TV.

Human exposure to PFRs via ingestion of dust

Table 2 gives estimates of exposure to PFRs for both UK adults and young children under three scenarios: (a) low-end, where dust contaminated at the 5th percentile concentration was ingested at the average rate (2.6 mg and 41 mg day^{-1} for adults and children respectively – Wilson et al, 2013); (b) median, where dust contaminated at the median concentration was ingested at the average rate; and (c) high-end, where dust contaminated at the 95th percentile concentration was ingested at the high-end rate (8.6 mg and 140 mg day^{-1} for adults and children respectively – Wilson et al 2013). Adults (70 kg) were assumed to spend 4.2%, 23.8%, and 72% of their time in cars, offices, and at home respectively (Harrad et al, 2008), with children (20 kg) spending 4.2%, 20.1%, and 75.7% of their time in cars, classrooms, and in the home (Harrad et al, 2010). In the absence of definitive data on the relative intake of dust in different microenvironments, dust ingestion was assumed pro-rata to the time spent in each microenvironment.

283 Reassuringly, even our high-end exposure estimates for young children are - even in the worst
284 scenario (for TDCIPP) - ~90 times lower than the health based limit value (HBLV) cited by Ali et
285 al (2012). However, we also note that our high-end exposure to TCIPP for a child is only ~5 times
286 lower than the HBLV cited by Saito et al (2007). Moreover, these HBLVs have no legislative
287 standing, current knowledge of the human health impacts of PFRs is based on somewhat dated
288 information, and new toxicological information may reduce the margin of safety. Furthermore, the
289 margin of safety will be reduced commensurately if the body weight of the notional child receptor
290 was assumed lower – e.g. 12 kg as used by Ali et al (2012). As a further caveat, our exposure
291 estimates consider dust ingestion only, and additional exposure via other pathways such as diet,
292 inhalation, and dermal uptake (both from dust and direct contact with PFR-treated items), will
293 narrow further the margin of safety.
294
295 Overall, this study demonstrates that contamination of UK indoor dust with PFRs is substantial,
296 exceeding by orders of magnitude that observed for PBDE congeners prevalent in the Penta- and
297 Octa-BDE formulations, and being of similar magnitude to that seen for BDE-209. Studies to
298 characterise other pathways of PFR exposure and the potential adverse health effects of such
299 exposure are recommended.
300
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305
306 **References:**
307 • Abdallah, M. A-E., Covaci, A. 2014. Organophosphate Flame Retardants in Indoor Dust from
308 Egypt: Implications for Human Exposure. *Environ. Sci. Technol.*, 48: 4782−4789.

309 • Ali, N., Dirtu, A. C., Van den Eede, N., Goosey, E., Harrad, S., Neels, H., 't Mannetje, A.,
310 Coakley, J., Douwes, J., Covaci, A. 2012. Occurrence of Alternative Flame Retardants in Indoor
311 Dust from New Zealand: Indoor Sources and Human Exposure Assessment. *Chemosphere* 88:
312 1276–1282.
313 • Ali, N., Ali, L., Mehdi, T., Dirtu, A. C., Al-Shammari, F., Neels, H., Covaci, A. 2013. Levels and
314 profiles of organochlorines and flame retardants in car and house dust from Kuwait and
315 Pakistan: implication for human exposure via dust ingestion. *Environ*. *Int*., 55: 62–70.
316 • Araki, A., Saito, I., Kanazawa, A., Morimoto, K., Nakayama, K., Shibata, E., Tanaka, M.,
317 Takigawa, T., Yoshimura, T., Chikara, H., Saijo, Y., Kishi, R. 2014. Phosphorus flame retardants
318 in indoor dust and their relation to asthma and allergies of inhabitants. Indoor Air, 24: 3–15.
319 • Bergh, C., Åberg, M. K., Svartengren, M., Emenius, G., Östman, C. 2011a. Organophosphate
320 and phthalate esters in indoor air: a comparison between multi-storey buildings with high and
321 low prevalence of sick building symptoms. *J*. *Environ*. *Monit*. 13: 2001–2009.
322 • Bergh, C., Torgrip, R., Emenius, G., Östman, C. 2011b. Organophosphate and phthalate esters in
323 air and settled dust – a multi-location indoor study. *Indoor Air*, 21: 67–76.
324 • Bolgar, M., Hubball, J., Groeger, J., Meronek, S. 2008. Handbook for the Chemical Analysis of
325 Plastic and Polymer Additives. CRC Press Taylor & Francis Group, New York (2007025615).
326 • Brandsma, S. H., de Boer, J., Cofino, W. P., Covaci, A., Leonards, P. E. G. 2013.
327 Organophosphorus flame-retardant and plasticizer analysis, including recommendations from
328 the first worldwide interlaboratory study. *TRAC*, 43: 217-228
329 • Brandsma, S. H., de Boer, J., van Velzen, M. J. M., Leonards, P. E. G. 2014. Organophosphorus
330 flame retardants (PFRs) and plasticizers in house and car dust and the influence of electronic
331 equipment. *Chemosphere*, 116: 3–9.
332 • Brommer, S., Harrad, S., Van den Eede, N., Covaci, A. (2012) Concentrations of
333 Organophosphate Esters and Brominated Flame Retardants in German Indoor Dust Samples. *J*.
334 *Environ*. *Monit*. 14: 2482-2487.

- Camarasa, J. G., Serra-Baldrich, E. 1992. Allergic contact dermatitis from triphenyl phosphate. *Contact Dermatitis*, 26: 264-265.
- Carignan, C. C., McClean, M. D., Cooper, E. M., Watkins, D. J., Fraser, A. J., Heiger-Bernays, W., Stapleton, H. M., Webster, T. F. 2013. Predictors of tris(1,3-dichloro-2-propyl) phosphate metabolite in the urine of office workers. *Environ*. *Int*., 55: 56–61.
- Cequier, E., Ionas, A. C., Covaci, A., Marcé, R. M., Becher, G., Thomsen, C. 2014. Occurrence of a Broad Range of Legacy and Emerging Flame Retardants in Indoor Environments in Norway. *Environ*. *Sci*. *Technol*. 2014, 48, 6827−6835.
- Dirtu, A. C., Ali, N., Van den Eede, N., Neels, H., Covaci, A. 2012. Country specific comparison for profile of chlorinated, brominated and phosphate organic contaminants in indoor dust. Case study for Eastern Romania, 2010. *Environ*. *Int*., 49: 1−8.
- Dishaw, L.V., Powers, C.M., Ryde, I.T., Roberts, S.C., Seidler, F.J., Slotkin, T.A., Stapleton, H.M. 2011. Is the PentaBDE replacement, tris (1,3-dichloropropyl) phosphate (TDCPP), a developmental neurotoxicant? Studies in PC12 cells. *Toxicol*. *Appl*. *Pharmacol*., 256: 281–289.
- Dodson, R. E., Perovich, L. J., Covaci, A., Van den Eede, N., Ionas, A. C., Dirtu, A. C., Brody, J. G., Rudel, R. A. 2012. After the PBDE Phase-Out: A Broad Suite of Flame Retardants in Repeat House Dust Samples from California. *Environ*. *Sci*. *Technol*., 46: 13056−13066.
- Environment Agency. 2009. Environmental Risk Evaluation Report: 2- Ethylhexyl diphenyl phosphate (CAS No. 1241-94-7) [online]. Available from: https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/290842/scho0809bqty-e-e.pdf [Accessed 12 July 2012]
- European Union (2008) Tris[2-chloro-1-(chloromethyl)ethyl] phosphate (TDCP) Risk Assessment Report [online]. Available from: https://echa.europa.eu/documents/10162/13630/trd_rar_ireland_tdcp_en.pdf [Accessed 5 May 2012]
- Fan, X., Kubwabo, C., Rasmussen, P. E., Wu, F. 2014. Simultaneous determination of thirteen

organophosphate esters in settled indoor house dust and a comparison between two sampling techniques. *Sci Tot*. *Environ*., 491-492: 80–86.

- Fromme, H., Lahrz, T., Kraft, M., Fembacher, L., Mach, C., Dietrich, S., Burkardt, R., Völkel, W., Göen, T. 2014. Organophosphate flame retardants and plasticizers in the air and dust in German daycare centers and human biomonitoring in visiting children (LUPE 3). *Environ*. *Int*., 71: 158–163.
- Harrad, S., Ibarra, C., Abdallah, M. A., Boon, R., Neels, H., Covaci, A. (2008) Concentrations of brominated flame retardants in dust from United Kingdom cars, homes, and offices: Causes of variability and implications for human exposure. *Environ*. *Int*. 34: 1170–1175.
- Harrad, S., Goosey, E., Desborough, J. Abdallah, M. A-E., Roosens, L., Covaci, A. (2010) Dust from UK primary school classrooms and daycare centers: The significance of dust as a pathway of exposure of young UK children to Brominated Flame Retardants and Polychlorinated Biphenyls. *Environ*. *Sci*. *Technol*. 44: 4198–4202.
- Jonsson, O. B., Nilsson, U.L. 2003. Determination of organophosphate ester plasticisers in blood donor plasma using a new stir-bar assisted microporous membrane liquid-liquid extractor. *J*. *Sep*. *Sci*., 26: 886–892.
- Kanazawa, A., Saito, I., Araki, A., Takeda, M., Ma, M., Saijo, Y., Kishi, R. 2010. Association between indoor exposure to semi-volatile organic compounds and building-related symptoms among the occupants of residential dwellings. *Indoor Air*, 20: 72-84.
- Marklund, A. Andersson B. Haglund, P. 2003. Screening of organophosphorus compounds and their distribution in various indoor environments. *Chemosphere* 53: 1137–1146.
- Meeker, J. D., Stapleton, H.M. 2010. House dust concentrations of organophosphate flame retardants in relation to hormone levels and semen quality parameters. *Environ*. *Hlth*. *Perspect*., 118: 318-323.
- Saito, I., Onuki, A., Seto. H. 2007. Indoor organophosphate and polybrominated flame retardants in Tokyo. *Indoor Air,* 17: 28–36.

- Stapleton, H. M., Klosterhaus, S., Eagle, S., Fuh, J., Meeker, J. D., Blum, A., Webster, T. F. 2009. Detection of organophosphate flame retardants in furniture foam and U.S. house dust. *Environ. Sci. Technol.* 43: 7490–7495.
- Stapleton, H. M., Sharma, S., Getzinger, G., Ferguson, P. L., Gabriel, M., Webster, T. F., Blum, A. 2012. Novel and High Volume Use Flame Retardants in US Couches Reflective of the 2005 PentaBDE Phase Out. *Environ. Sci. Technol.* 46: 13432–13439.
- Tajima, S., Araki, A., Kawai, T., Tsuboi, T., Ait Bamai, Y., Yoshioka, E., Kanazawa, A., Cong, S., Kishi, R. 2014. Detection and intake assessment of organophosphate flame retardants in house dust in Japanese dwellings. *Sci. Tot. Environ.*, 478: 190–199.
- Umezu, T., Yonemoto, J., Soma, Y., Suzuki, T. 1998. Tris(2-chloroethyl) phosphate increases ambulatory activity in mice. Pharmacological analyses of its neurochemical mechanism. *Toxicol. Appl. Pharmacol.*, 148: 109–116.
- Van den Eede, N., Dirtu, A. C., Neels, H., Covaci, A. 2011. Analytical developments and preliminary assessment of human exposure to organophosphate flame retardants from indoor dust. *Environ. Int.* 37: 454–461.
- Van der Veen, I., de Boer, J. 2012. Phosphorus flame retardants: Properties, production, environmental occurrence, toxicity and analysis. *Chemosphere*, 88: 1119−1153.
- Wilson, R., Jones-Otazo, H., Petrovic, S., Mitchell, I., Bonvalot, Y., Williams, D., Richardson, G. M. 2013. Revisiting Dust and Soil Ingestion Rates Based on Hand-to-Mouth Transfer. *Hum. Ecol. Risk Ass.* 19: 158–188.

Table 1: Statistical Summary of Concentrations (μg g^{-1}) of PFRs in UK Car, Classroom, Living Room and Office Dust Compared with Concentrations Recorded Elsewhere

Concentration/ Microenvironment	Statistical Parameter	TNBP	TCEP	TCIPP	TPHP	EHDPP	TDCIPP	TMPP
Living Room (n=32; this study)	Minimum	<0.03	<0.06	3.7	0.49	0.18	0.06	<0.01
	Median	<0.03	0.81	21	3.3	1.6	0.71	0.02
	Average	0.04	2.2	29	10	2.6	2.0	2.0
	Maximum	0.09	28	100	110	130	14	14
Belgium (n=33; Van den Eede et al, 2011)	Median	0.25	0.49	4.8	2.0	-	0.57	-
Canada (n=134; Fan et al, 2014)	Median	0.25	0.80	1.4	1.7	0.54	2.7	2.6
Egypt (n=20; Abdallah and Covaci, 2014)	Median	0.017	0.022	0.028	0.067	0.042	0.072	-
Japan (n=148); (Araki et al, 2014)	Median	1.0	5.8	8.7	4.5	-	2.8	<4.0
Japan (n= 41; Kanazawa et al, 2010)	Median	1.4	7.5	18.7	5.4	-	4.0	<4.0
Japan (n=48; Tajima et al, 2014)	Median	<0.36	<0.65	0.74	0.87	-	<0.59	<4.0
The Netherlands (Brandsma et al, 2014)[a]	Median	0.032	1.3	1.3	0.82	0.35	0.28	0.11
New Zealand (n=34; Ali et al, 2012)	Median	0.08	0.11	0.35	0.6	-	0.23	0.12
Norway (n= 48; Cequier et al, 2014)	Median	0.055	0.41	2.7	0.98	0.62	0.50	0.31

Romania (n=47; Dirtu et al, 2012)	Median	0.045	0.10	0.86	0.50	-	0.06	0.50
USA (n=16; Dodson et al, 2012)	Median	<0.08	2.7	2.2	2.8	0.56	2.1	0.68
USA (n=50; Stapleton et al, 2009)	Geometric mean	-	-	0.57	7.4	-	1.9	-
Office (n=61; this study)	Minimum	<0.03	<0.06	3.6	0.56	0.15	<0.03	<0.01
	Median	<0.03	0.87	33	4.3	5.3	0.48	<0.01
	Average	0.10	5.0	44	8.2	10	2.1	0.33
	Maximum	1.3	160	230	50	81	51	5.3
Egypt (n=20, Abdallah and Covaci, 2014)	Median	0.023	0.031	0.080	0.073	0.048	0.049	-
Germany (n=10; Brommer et al, 2012)	Median	0.22	0.12	3.0	2.5	-	0.15	0.37
Sweden (n=10; Bergh et al, 2011b)	Median	0.2	6.7	19	5.3	1.0	17	0.6
USA (n=31; Carignan et al, 2013)	Geometric mean	-	-	-	-	-	6.1	-
Car (n=21; this study)	Minimum	<0.03	<0.06	2.4	0.27	0.29	0.11	<0.01
	Median	<0.03	1.23	53	3.3	2.2	31	0.59
	Average	0.14	1.95	83	15	2.9	110	1.0
	Maximum	1.2	8.7	370	170	11	740	5.6
Egypt (n=20; Abdallah and Covaci, 2014)	Median	0.059	0.13	0.29	0.14	0.054	0.061	-
Germany (n=12; Brommer et al, 2012)	Median	0.015	0.28	3.2	7.5	-	21	-

Kuwait (n=15; Ali et al, 2013)	Median	0.73	1.8	31	1.8	-	7.6	-
The Netherlands (n=8; Brandsma et al, 2014)[b]	Median	<0.013	0.6	4.3	2.4	0.75	110	1.4
Pakistan (n=15; Ali et al, 2013)	Median	0.018	0.075	0.10	0.25	-	0.029	-
USA (n=31; Carignan et al, 2013)	Geometric mean	-	-	-	-	-	12.5	-
Classroom (n = 28; this study)	Minimum	<0.03	<0.06	1.7	0.22	0.30	0.04	<0.01
	Median	0.12	0.86	16	4.1	29	0.51	<0.01
	Average	0.17	1.5	33	12	50	1.1	0.05
	Maximum	0.46	8.3	210	90	470	10	5.8
Germany (n=63; Fromme et al, 2014)	Median	<0.3	0.4	2.7	0.5	-	-	-
Norway (n=6; Cequier et al, 2014)	Median	0.044	1.2	2.0	1.5	2.3	1.5	0.056
Sweden (n=10; Bergh et al, 2011b)	Median	1.2	30	3.1	1.9	0.8	9.1	0.4

[a]Sampled around electronics
[b]Sampled from car seats

Table 2: Daily Human Exposure (ng/kg body weight[a]) to PFRs via Dust Ingestion

Exposure Scenario/PFR	TNBP	TCEP	TCIPP	TPHP	EHDPP	TDCIPP	TMPP	ΣPFR
Adult – Low	<0.01	<0.01	0.22	0.03	0.02	<0.01	<0.01	0.28
Adult – Median	<0.01	0.03	0.92	0.13	0.09	0.07	<0.01	1.3
Adult – High	0.02	1.3	13	5.6	5.1	3.1	0.19	28
Child – Low	<0.01	0.29	10	1.3	0.86	0.27	<0.01	13
Child – Median	0.08	1.7	43	7.0	14	4.0	0.08	70
Child – High	1.3	45	740	360	420	170	11	1740
HBLV[b]	24,000	22,000	80,000 (3,600[c])	70,000	-	15,000	13,000	-

[a]Adult body weight assumed to be 70 kg; child body weight assumed to be 20 kg

[b]Health based limit values are those reported by Ali et al (2012), except for [c] which is that cited by Saito et al (2007)

Figure 1: Median Concentrations of PFRs (µg g^{-1}) in UK Classroom, Car, Living Room, and Office Dust

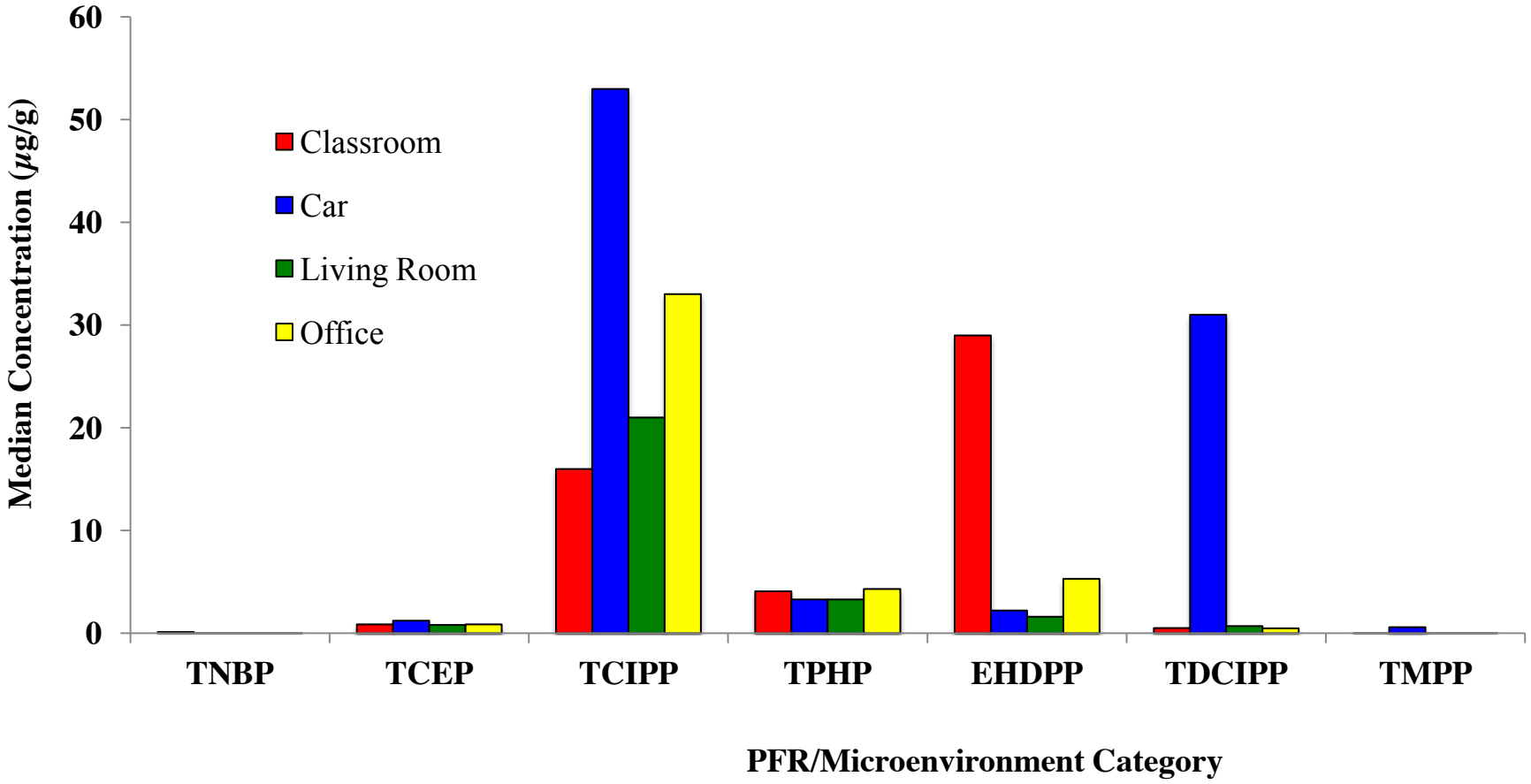
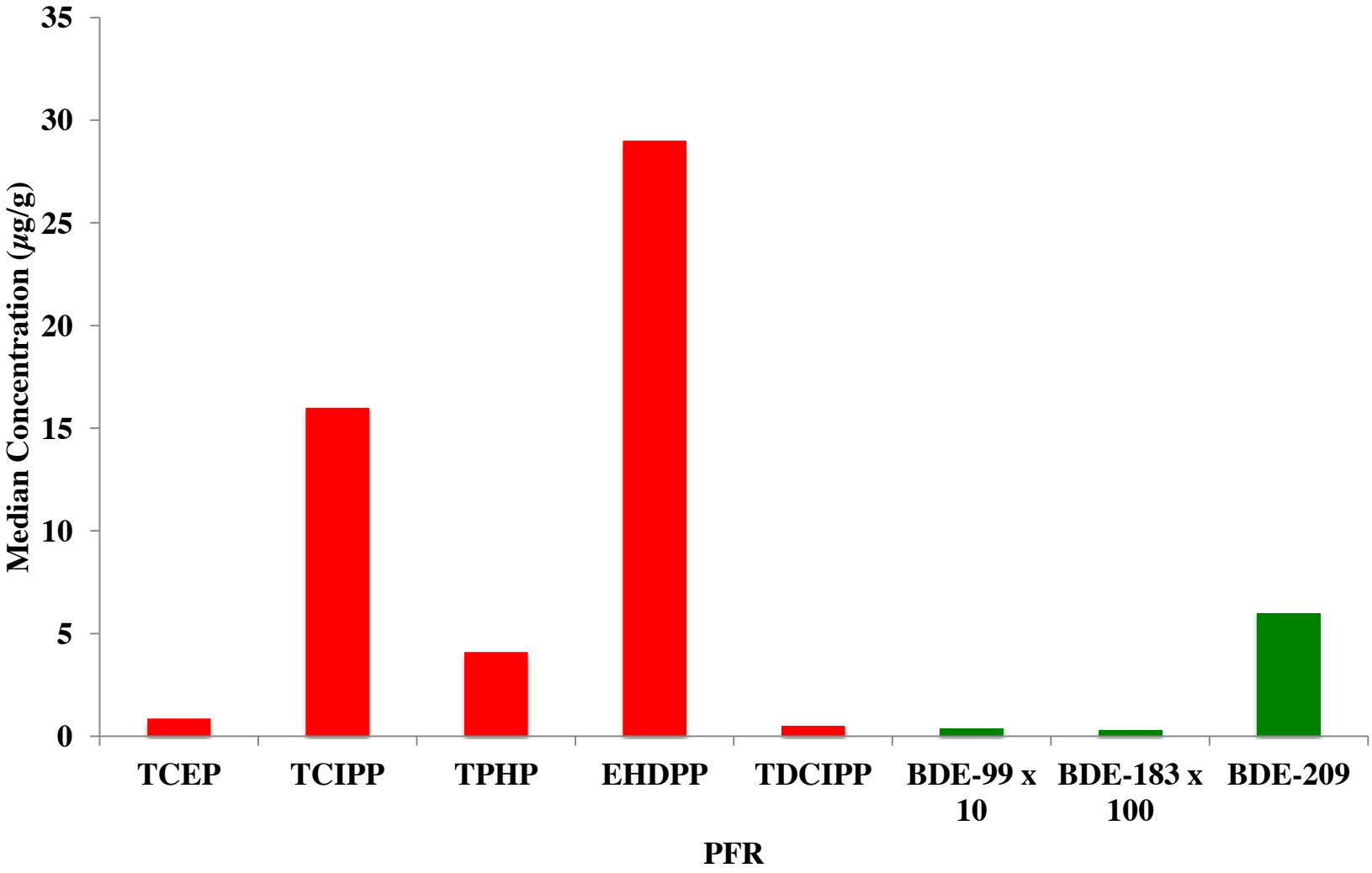


Figure 2: Median Concentrations of Selected PFRs and PBDEs in UK Classroom Dust



SUPPLEMENTARY DATA

SOURCES AND HUMAN EXPOSURE IMPLICATIONS OF CONCENTRATIONS OF ORGANOPHOSPHATE FLAME RETARDANTS IN DUST FROM UK CARS, CLASSROOMS, LIVING ROOMS, AND OFFICES

Sandra Brommer and Stuart Harrad

Table SD-1 m/z Values monitored for Target PFRs

Compound	Quantification Ion	Identification Ion
TNBP	211	155
TCEP	249	251
TCIPP	277	279
TPHP	326	325
TDCIPP	381	379
EHDPP	251	250
TMPP	368	367
D_{27}-TNBP	103	167
D_{15}-TPHP	341	339
TAP	239	169

Table SD-2: Summary of Concentrations (μg g^{-1}) of PFRs Detected in SRM2585 in this Study (n=56) and in an Interlaboratory Study (Brandsma et al, 2013)

Parameter/PFR	TNBP	TCEP	TCIPP	TDCIPP	EHDPP	TPHP	TMPP
Average (this study)	0.18	0.79	0.90	1.83	0.82	0.98	0.93
Minimum (this study)	0.15	0.65	0.76	1.48	0.70	0.81	0.79
Maximum (this study)	0.22	1.0	1.04	2.05	0.93	1.1	1.1
σ_n (this study)	0.02	0.11	0.07	0.14	0.06	0.06	0.09
RSD (this study - %)	10	14	7.8	7.9	7.1	6.4	10
Assigned Value[a]	0.269	0.792	0.944	1.56	0.963	1.1	0.843

[a] Assigned values from Brandsma et al, 2013
[b] Indicative value from Brandsma et al, 2013

Table SD-3 Concentrations (μg g^{-1}) of PFRs in Individual Dust Samples in this Study

(a) Living Room Dust

TNBP	TCEP	TCIPP	TPHP	EHDPP	TDCIPP	TMPP
<0.03	0.44	100	1.1	0.39	7.0	<0.01
<0.03	5.4	38	0.75	1.1	0.67	<0.01
0.09	0.03	24	3.7	29	1.2	0.14
0.07	28	18	0.72	1.4	1.6	0.27
<0.03	0.60	32	12	6.0	0.85	0.91
0.07	1.5	18	0.68	1.2	0.62	0.36
0.07	<0.06	6.6	0.49	0.31	0.15	0.26
0.06	0.59	24	1.1	3.2	0.11	0.46
<0.03	8.3	21	1.5	1.5	2.0	0.37
0.09	0.61	20	0.84	0.87	0.16	0.35
0.07	3.9	27	5.4	16	2.3	<0.01
<0.03	0.40	29	0.77	0.45	14	<0.01
<0.03	0.18	9.8	0.77	0.34	0.66	<0.01
<0.03	0.58	19	2.8	1.3	1.3	0.77
0.05	0.51	24	2.0	0.65	11	0.13
<0.03	2.5	4.2	2.2	0.18	0.20	<0.01
<0.03	0.34	3.7	8.50	15	0.16	<0.01
<0.03	0.24	16	2.9	2.1	0.09	<0.01
<0.03	0.92	9.1	11	15	0.06	<0.01
<0.03	1.8	7.0	71	131	0.13	44
<0.03	2.0	7.7	3.7	3.0	2.4	<0.01
<0.03	0.55	11	110	0.82	0.75	0.30
<0.03	1.8	79	8.6	11	0.27	<0.01
0.09	0.97	5.7	11	6.7	3.3	1.6
<0.03	0.92	12	4.7	7.9	0.15	<0.01
<0.03	0.26	14	11	16	2.3	<0.01
<0.03	0.45	43	4.0	0.47	2.1	<0.01
0.05	1.9	47	0.74	0.84	0.85	1.28
<0.03	1.5	43	6.1	12	0.62	0.25
0.09	1.1	41	0.57	1.6	0.16	0.03
<0.03	0.71	65	29	67	0.12	<0.01
<0.03	1.1	100	5.0	0.43	7.9	<0.01

(b) Car Dust

TNBP	TCEP	TCIPP	TPHP	EHDPP	TDCIPP	TMPP
<0.03	<0.06	10	1.2	0.98	16	0.78
<0.03	0.62	72	6.4	3.3	24	0.42
0.25	1.5	48	5.3	1.5	31	0.95
<0.03	0.72	170	8.2	1.1	200	1.8
<0.03	0.97	91	4.8	2.2	350	<0.01
0.08	1.8	50	1.8	3.7	7.3	0.59
<0.03	8.7	73	7.0	2.0	3.2	5.6
0.07	0.83	18	2.6	2.3	1.5	1.2
1.2	0.40	2.4	0.77	0.29	1.0	<0.01
0.96	0.61	20	172	1.1	741	<0.01
<0.03	7.7	31	3.3	11	8.4	1.6
0.09	0.23	8.0	1.7	5.7	0.11	0.05
<0.03	2.4	370	1.3	2.1	31	0.07
<0.03	1.5	69	76	1.1	3.8	<0.01
<0.03	0.30	54	0.74	0.49	32	0.06
<0.03	1.6	300	3.4	4.4	140	0.51
<0.03	0.43	160	1.6	0.64	130	<0.01
0.15	1.2	46	12	6.0	410	2.2
<0.03	5.1	85	3.5	3.1	100	0.91
<0.03	1.4	53	2.3	2.6	63	0.74
<0.03	3.0	22	0.27	6.4	1.5	4.0

(c) Office Dust

TNBP	TCEP	TCIPP	TPHP	EHDPP	TDCIPP	TMPP
<0.03	1.7	33	6.5	1.9	0.05	<0.01
0.24	0.87	55	1.4	0.57	3.0	0.18
<0.03	0.80	97	2.7	7.7	0.40	<0.01
0.27	0.82	57	19	35	0.46	0.56
0.14	3.6	54	11	8.0	8.9	<0.01
<0.03	0.87	52	21	5.5	0.22	<0.01
<0.03	0.90	58	18	9.8	0.30	1.2
<0.03	1.4	82	7.4	13	0.53	<0.01
<0.03	0.67	19	3.5	3.0	0.21	<0.01
<0.03	0.42	10	3.8	0.94	0.06	1.2
<0.03	<0.06	17	2.3	5.9	0.13	<0.01
<0.03	<0.06	8.8	0.66	0.87	0.04	<0.01
<0.03	0.31	22	1.4	2.3	0.16	0.23
0.11	0.33	14	1.1	2.4	2.1	0.04
<0.03	0.18	18	2.1	4.7	0.35	<0.01
0.08	2.1	19	20	20	0.14	<0.01
0.02	0.23	24	1.7	4.1	1.2	<0.01
0.11	1.0	67	5.2	27	1.0	0.53
0.08	0.92	16	1.6	1.4	0.35	0.25
<0.03	5.7	48	44	22	51	<0.01
<0.03	0.77	23	3.6	4.2	1.1	0.08
<0.03	5.2	25	3.2	4.1	1.1	0.20
0.05	1.9	33	4.3	5.3	2.3	<0.01
<0.03	2.0	47	6.9	10	0.48	<0.01
0.97	1.0	52	4.7	3.1	1.5	<0.01
0.13	1.3	48	6.2	7.0	2.6	<0.01
0.15	<0.06	14	0.56	0.84	0.34	0.32
0.04	0.79	15	3.2	1.5	0.97	<0.01
0.05	0.37	10	1.3	1.2	0.26	<0.01
0.07	1.4	15	2.2	4.6	0.76	<0.01

0.04	1.3	48	7.8	9.8	1.0	<0.01
<0.03	0.37	39	6.5	3.0	2.9	5.2
0.07	1.0	61	6.5	34	0.41	<0.01
0.05	0.42	32	3.6	7.9	3.1	<0.01
<0.03	0.38	34	11	8.4	1.3	3.3
<0.03	0.37	25	7.2	2.6	1.1	<0.01
0.05	<0.06	8.9	2.3	2.8	0.39	<0.01
<0.03	<0.06	8.9	1.9	2.6	0.30	<0.01
0.04	0.44	19	31	3.4	0.22	<0.01
<0.03	0.24	25	1.4	2.3	3.4	<0.01
<0.03	0.30	230	3.1	3.5	0.53	<0.01
<0.03	1.5	17	7.7	12	1.7	1.3
0.05	0.63	46	2.8	5.8	1.1	0.33
<0.03	3.1	14	2.6	2.5	2.5	0.05
0.25	2.0	41	36	68	12	<0.01
<0.03	0.48	47	50	8.6	2.1	<0.01
0.03	3.8	19	31	81	<0.03	<0.01
<0.03	1.2	17	2.3	5.2	0.28	0.42
0.27	0.85	43	11	21	0.23	0.50
0.04	0.70	22	1.3	0.15	<0.03	<0.01
<0.03	1.0	140	5.5	8.0	0.83	<0.01
<0.03	3.1	17	1.5	3.7	<0.03	<0.01
<0.03	0.5	3.6	3.1	9.4	0.03	0.42
0.51	0.5	40	0.68	0.59	0.37	1.7
<0.03	2.2	35	5.4	4.5	0.32	<0.01
<0.03	2.6	29	2.0	6.2	0.59	<0.01
0.06	2.0	56	6.0	5.6	0.27	0.40
<0.03	22	220	9.9	15	5.7	0.09
<0.03	28	130	11	21	0.14	<0.01
1.30	23	110	7.7	14	0.82	0.10
0.13	160	51	10	24	0.36	1.4

(d) Classroom Dust

TNBP	TCEP	TCIPP	TPHP	EHDPP	TDCIPP	TMPP
0.08	2.1	150	6.8	68	2.47	0.07
0.04	0.63	19	1.8	56	1.06	0.25
0.33	0.84	16	1.6	28	1.04	<0.01
0.17	0.84	7.8	28	120	0.14	<0.01
<0.03	0.53	13	4.4	33	0.52	0.09
0.36	1.5	16	2.1	5.3	1.44	0.63
0.37	0.81	43	6.8	6.8	1.79	1.8
0.20	1.9	11	9.5	30	0.77	5.8
<0.03	1.9	210	5.5	29	0.51	<0.01
0.28	7.0	35	2.7	16	0.41	<0.01
0.27	0.87	15	3.8	6.2	0.61	<0.01
<0.03	0.50	1.7	0.4	0.6	10	<0.01
<0.03	<0.06	8.6	1.2	0.9	0.07	<0.01
0.46	0.84	34	1.4	2.8	0.77	0.76
0.20	0.40	11	11	86	0.35	0.53
0.08	1.7	8.1	3.2	2.0	0.20	0.34
0.39	0.28	41	2.0	6.5	1.2	0.19
0.34	0.98	20	36	70	0.36	<0.01
<0.03	0.24	5.6	0.2	0.3	0.04	<0.01
0.09	0.84	16	11	66	0.26	<0.01
0.06	1.6	5.0	18	120	0.21	<0.01
0.05	0.81	10	11	16	0.24	0.89
0.09	0.25	5.7	2.8	9.6	0.42	<0.01
0.18	1.4	32	3.1	37	0.44	0.65
0.04	1.6	4.3	3.3	59	0.08	<0.01
0.41	1.3	65	65	470	0.77	<0.01
0.13	1.3	28	9.8	53	0.74	1.45
0.12	8.3	110	90	8.9	2.91	<0.01